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COMPLETE SPECIFICATION

Process for the manufacture of 2:5-diarylamino-terephthalic Acids

5 We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention is based on the observation that 2:5-diarylamino-terephthalic acids can be obtained in a simple manner and in good yield by heating a 2:5-diarylamino-dihydro-terephthalic acid ester with nitrobenzene and an alkali metal hydroxide in a water-soluble alcohol, if desired, filtering the reaction mixture, and then acidifying it with an aqueous or alcoholic mineral acid solution of 15 to 80% strength and washing the precipitated 2:5-diarylamino-terephthalic acid with a water-soluble alcohol.

20 The 2:5-diarylamino-dihydroterephthalic acid esters to be used as starting materials contain as aryl residues, for example, naphthalene residues or preferably benzene residues which may contain substituents such, for example, as halogen atoms or alkyl, alkoxy, hydroxyl or nitro groups. The aforementioned diarylamino-dihydroterephthalic acid esters can be obtained by condensing 1 molecular proportion of a succinylsuccinic acid ester with 2 molecular proportions of an aryl-amine, for example, aniline, paratoluidine, 4-chloroaniline, 2:4-dichloroaniline or 4-methoxyaniline. This condensation is 35 advantageously performed in an organic solvent in the presence of a mineral acid, more especially hydrochloric acid, as catalyst and a slight excess of the amine, for example amounting to 5 to 10%. It is of advantage 40 to use as organic solvent the same alcohol as is to be used for carrying out the process of the invention; in this case the resulting

dihydro ester can be oxidised and hydrolysed without intermediate isolation in the same vessel to yield the diarylamino-terephthalic acid. 45

The oxidation according to the present invention is advantageously carried out with 0.5 to 2 molecular proportions of nitrobenzene and 2 to 3 molecular proportions of an alkali metal hydroxide, for example potassium hydroxide or more especially sodium hydroxide, for every molecular proportion of dihydro ester. The alkali metal hydroxide is advantageously added in the form of a concentrated aqueous solution or of an alcoholic, for example methanolic, solution. The oxidation begins only after the addition of the alkali metal hydroxide. 55

It is of advantage to use as water-soluble alcohol an aliphatic alcohol containing 1 to 3 carbon atoms, for example methanol or isopropanol, or a glycol or glycol monoalkyl ether. For every part of dihydro ester it is of advantage to use 1 to 20 parts of alcohol. 60 The recovery of the alcohol is rendered easier by using as alcohol the same alcohol as is to be eliminated from the original ester group in the course of the hydrolysis. The reaction is advantageously performed at the boiling temperature of the alcohol, thus at about 60° to 130° C. The 2:5-diarylamino-dihydro-terephthalic acid ester is oxidised to the alkali metal salt of 2:5-diarylamino-terephthalic acid, accompanied by hydrolysis of the carbalkoxy groups. 65 70 75

Working up according to the present process consists in acidifying the aqueous-alcoholic solution of the alkali metal salt of 2:5-diarylamino-terephthalic acid with an aqueous or alcoholic solution of 15 to 80% strength of a mineral acid, advantageously after having first filtered the former. Suitable mineral acids are sulphuric or phosphoric 80

acid, or more especially hydrochloric acid advantageously an aqueous hydrochloric acid solution of 20 to 40% strength. The amount of acid to be added is advantageously such that the reaction mixture reacts acid to Congo red. The 2:5-diarylamino-terephthalic acid is obtained in a coarsely crystalline form which is easy to filter. After having been filtered off, the acid is washed according to the present process with a water-soluble alcohol, advantageously with the same alcohol as has been used as solvent for the oxidation. It is of advantage to continue the washing until the filtrate is only of a pale yellow colour. As a rule this can be achieved with about half the amount of alcohol required for the oxidation and hydrolysis. To remove any water-soluble salts from it the precipitate is then washed in the conventional manner with water and advantageously dried *in vacuo*.

When commercial raw materials are used, the resulting acid may still contain a small amount of insoluble impurities which are advantageously removed by filtering the diarylamino-terephthalic acid in the form of an aqueous solution of a dialkali metal salt thereof and precipitating the diarylamino-terephthalic acid again by acidifying the filtrate.

This operation can be dispensed with when the alcoholic alkaline solution of the dialkali metal salt of the diarylamino-terephthalic acid resulting from the oxidation and hydrolysis has been filtered prior to the acidification.

By the present process the diarylamino-terephthalic acids are obtained in outstanding yields and excellent purity. The quinacridones prepared therefrom are distinguished by the great purity of their tints.

The following examples illustrate the invention, the parts and percentages being by weight unless otherwise stated.

EXAMPLE 1

A mixture of 12.8 parts of succinylsuccinic acid diethyl ester, 11.5 parts of para-toluidine in 150 parts by volume of absolute alcohol containing 5 drops of concentrated hydrochloric acid is refluxed and stirred for about 10 hours, whereupon 2:5-dihydro-di-(para-toluidino)-terephthalic acid diethyl ester crystallises out rapidly in a substantially colourless form from the hot reaction mixture. The suspension is allowed to cool slightly, then mixed with 6.5 parts of nitrobenzene and 13 parts by volume of sodium hydroxide solution of 30% strength, refluxed for a further 2 hours; within a short time a pale, yellowish clear solution is obtained. The solution is filtered while still hot until it is clear and 20 parts by volume of concentrated hydrochloric acid are then stirred in until the solution displays an acid reaction to Congo red. After stirring for a short time the precipitated blue-violet 2:5-di-(para-toluidino)-terephthalic acid is suctioned

off, washed with about 200 parts by volume of hot alcohol and then with water, and dried *in vacuo* at 80 to 90° C. Yield: 17.82 parts=94.9% of the theoretical.

When, as has been usual hitherto, the yellow solution of the disodium salt of 2:5-di-(para-toluidino)-terephthalic acid is diluted with water in the course of the working up, and the solution is filtered until it is clear and then acidified, there is obtained a 2:5-di-(para-toluidino)-terephthalic acid which still contains some impurities that can hardly be removed by subsequent washing with alcohol.

EXAMPLE 2

100 parts of succinic acid diethyl ester are converted into succinylsuccinic acid ester by one of the methods described in the literature, for example by condensation with 14.5 parts of sodium in absolute alcohol. The resulting crude disodium salt of succinylsuccinic acid diethyl ester is dried, somewhat disintegrated, treated with 350 parts by volume of methanol and 84 parts of aniline hydrochloride, and the mixture is heated to the boil with stirring under reflux. After about one hour 31 parts by volume of nitrobenzene are added and the mixture is maintained at a gentle boil for about 4 to 6 hours after which time an orange-yellow suspension is obtained. At an internal temperature of 55 to 60° C. 85 parts by volume of sodium hydroxide solution of 30% strength are slowly added dropwise and the mixture is again refluxed for about 1 to 2 hours. While still hot, the resulting yellow, slightly turbid solution is acidified with 120 parts by volume of concentrated hydrochloric acid, cooled to room temperature and the dark-violet product is suctioned off. After washing three times with 70 parts by volume of methanol the filter residue is dissolved in hot water with 50 parts by volume of sodium hydroxide solution of 30% strength and freed by filtration from traces of impurities. The clear, yellow filtrate is then treated at 70° C. with 70 parts by volume of concentrated hydrochloric acid and the resulting violet precipitate is stirred for a short time, suctioned off, washed free from acid and salt with hot water, and dried *in vacuo* at 90 to 100° C. 80.0 grams of violet-red 2:5-dianilino-terephthalic acid are obtained, corresponding to 80% of the theoretical yield calculated on succinic acid diethyl ester.

The yield and the quality of the final product are substantially identical when instead of the methanol used above an equal volume of ethanol or isopropanol is used.

EXAMPLE 3

A mixture of 51.2 parts of succinylsuccinic acid diethyl ester, 38 parts by volume of aniline, 1.3 parts of aniline hydrochloride, 200 parts by volume of methanol and 21.5

parts by volume of nitrobenzene is stirred for 4 hours under reflux. The resulting orange suspension is treated at room temperature with 55 parts by volume of sodium hydroxide solution of 30% and then boiled for about 1 hour longer. A small amount of a filter assistant is added and the mixture is filtered hot until it is clear and the filter residue is rinsed with a small amount of hot methanol. While still hot, the yellow filtrate is acidified with 75 parts by volume of concentrated hydrochloric acid, the resulting precipitate is stirred for a short time, suction-filtered and washed by being covered three times with methanol. Further working up is carried out depending on the purpose for which the final product is to be used, for example by one of the following methods:—

(1) When the filter cake is dried *in vacuo* as it is, it yields pure 2:5-dianilino-terephthalic acid containing a small amount of sodium chloride. In contrast thereto the dianilino-terephthalic acid is obtained in a salt-free form when the suction filter cake is washed with water before being dried.

(2) When the reaction product is dissolved in water and about 80 parts by volume of sodium hydroxide solution of 30% strength, a deep yellow solution of the disodium salt of dianilino-terephthalic acid is obtained. When the latter solution is acidified, the free dianilino-terephthalic acid precipitates from it, while by salting out with about 25 parts of sodium chloride per 100 parts by volume of liquid the golden yellow crystalline disodium salt is obtained. The latter salt can be washed with sodium chloride solution and then dried, or it can be converted into pure dianilino-terephthalic acid by being taken up in water and acidified.

The yield of dianilino-terephthalic acid of 100% purity is in each case at least equal to 92% of the theoretical calculated on succinylo-succinic acid diethyl ester. The yield does not depend on the moment when nitrobenzene is added to the reaction mixture provided that the nitrobenzene is not added considerably later than the 55 parts by volume of sodium hydroxide solution. On the other hand, the early addition of nitrobenzene to a relatively concentrated reaction batch causes a noticeable dilution of the reaction mixture.

tion of 30% strength are added dropwise, the mixture is refluxed for about one hour longer and then, while still hot, acidified with 75 parts by volume of concentrated hydrochloric acid. The coarsely crystalline 2:5-di-(para-anisidino)-terephthalic acid is suctioned off, washed with alcohol, then dissolved in a mixture of hot water and about 40 parts by volume of sodium hydroxide solution of 30% strength and then filtered until it is clear. Addition of sodium chloride to the solution precipitates the disodium salt which forms orange-red crystals, while an addition of 50 to 60 parts by volume of concentrated hydrochloric acid precipitates the dark-violet free dicarboxylic acid. The yield amounts to 94% of the theoretical.

By replacing in the above example the 54 parts of para-anisidine by an equimolecular amount of para-toluidine or para-chloraniline or ortho-chloraniline, there is obtained the 2:5-di-(para-toluidino)-terephthalic acid or respectively the 2:5-di-(para-chlor-anilino)-terephthalic acid or the 2:5-di-(ortho-chlor-anilino)-terephthalic acid in a yield corresponding in each case to 90 to 95% of the theoretical.

EXAMPLE 5

12.8 parts of succinylo-succinic acid diethyl ester and 9.77 parts of aniline in 100 parts by volume of absolute alcohol in the presence of a few drops of concentrated hydrochloric acid are condensed to form the dihydro-dianilino-terephthalic acid diethyl ester by being refluxed for several hours. The resulting suspension is allowed to cool slightly and then treated with 6.5 parts of nitrobenzene and 13.5 parts by volume of concentrated sodium hydroxide solution. On further refluxing a deep yellow solution of the disodium salt of dianilino-terephthalic acid is very rapidly obtained. 10 parts of kieselguhr are added, the whole is filtered until it is clear, and the yellow filtrate is rendered acid to Congo red at about 70° C. The dark-violet suspension is allowed to cool to room temperature, suction-filtered, washed with 50 parts by volume of alcohol and then with 200 parts of hot water and dried *in vacuo* at 90 to 100° C. Yield: 16.4 parts (94.2% of the theoretical) of 2:5-dianilino-terephthalic acid.

EXAMPLE 6

A mixture of 25.6 parts of succinylo-succinic acid diethyl ester, 25.8 parts of meta-anisidine, 500 parts by volume of absolute isopropanol and 10 to 15 drops of concentrated hydrochloric acid is condensed to form dihydro-di-(meta-anisidino)-terephthalic acid ester by being stirred under reflux. The reaction mixture is then allowed to cool to room temperature, whereupon it forms a weakly orange coloured suspension which is treated with 13 parts of nitrobenzene and

EXAMPLE 4

When a mixture of 51.2 parts of succinylo-succinic acid diethyl ester, 54 parts of para-anisidine, 400 parts by volume of absolute alcohol, 21.5 parts by volume of nitrobenzene is stirred in the presence of about 10 to 20 drops of concentrated hydrochloric acid for 6 hours under reflux, a reddish suspension of dihydro-2:5-di-(para-anisidino)-terephthalic acid diethyl ester is obtained. After cooling, 55 parts by volume of sodium hydroxide solu-

27 parts by volume of sodium hydroxide solution of 30% strength; it is then heated to 80 to 85° on a water bath and forms already during this heating a clear, deep yellow solution from which on boiling a small amount of the yellow disodium salt of di-(meta-anisidino)-terephthalic acid soon separates out. Boiling for about 1 to 2 hours completes the reaction, whereupon the thin yellow suspension is rendered acid to Congo red with concentrated hydrochloric acid. The whole is cooled to 20° C., suction-filtered and the filter cake is washed with cold isopropanol. The crude product is dissolved in hot water containing sodium carbonate, the solution is filtered, and from the clear yellow filtrate the disodium salt of di-(meta-anisidino)-terephthalic acid is salted out in the form of yellow crystals with sodium chloride. The crystals are suctioned off, washed with saturated sodium chloride solution and then dissolved in 1000 parts by volume of water heated at 80° C. By acidification with 40 parts by volume of hydrochloric acid the violet di-(meta-anisidino)-terephthalic acid is precipitated and then isolated in the conventional manner. Yield: 37.8 parts=92.6% of the theoretical.

EXAMPLE 7

A mixture of 25.6 parts of succinylsuccinic acid diethyl ester, 27.1 parts of meta-chloroaniline, 15 drops of concentrated hydrochloric acid and 500 parts by volume of absolute alcohol is converted by stirring for several hours under reflux into a yellow suspension of dihydro-di-(meta-chloroanilino)-terephthalic acid diethyl ester. 13 parts of nitrobenzene and 27 parts by volume of sodium hydroxide solution of 30% strength are then added at 50° C. and the mixture is refluxed for another 2 hours. The yellow solution is filtered to remove traces of dark impurities, rendered acid to Congo red with 40 parts by volume of concentrated hydrochloric acid, stirred for a short time, and the red-violet precipitate is suctioned off, washed with a small amount of alcohol and thoroughly with water and dried *in vacuo* at 80 to 90° C. Yield: 38.15 parts=91.4% of the theoretical.

EXAMPLE 8

A mixture of 12.8 parts of succinylsuccinic acid diethyl ester, 13 parts of para-anisidine, 5 drops of concentrated hydrochloric acid and 150 parts by volume of methanol is stirred under reflux for about 10 hours. The light-beige suspension is allowed to cool slightly, treated with 6.5 parts of nitrobenzene and 13.5 parts by volume of sodium hydroxide solution of 30% strength and again refluxed for 2 to 3 hours. The resulting yellow liquor is filtered until it is clear with the aid of kieselguhr, and the yellow filtrate is

rendered acid to Congo red with 25 parts by volume of concentrated hydrochloric acid. The whole is stirred for a short time, and the dark-violet 2:5-di-(para-anisidino)-terephthalic acid is suctioned off, washed with 3×50 parts by volume of methanol and then thoroughly with water and finally dried *in vacuo* at 90 to 100° C. Yield: 18.38 parts=90% of the theoretical.

When the 150 parts by volume of methanol are replaced by 150 parts by volume of isopropanol or 150 parts by volume of ethylene-glycol monomethyl ether, the reaction likewise being performed under reflux, the identical final product is obtained in a similar yield.

WHAT WE CLAIM IS:—

1. A process for the manufacture of 2:5-diarylamino-terephthalic acids, wherein a 2:5-diarylamino-dihydroterephthalic acid ester is heated with nitrobenzene and an alkali metal hydroxide in a water-soluble alcohol, the reaction mixture is acidified with an aqueous or alcoholic solution of a mineral acid of 15 to 80% strength, and the precipitated 2:5-diarylamino-terephthalic acid is washed with a water-soluble alcohol.

2. A process as claimed in Claim 1, wherein for every mol of diarylamino-dihydroterephthalic acid ester 0.5 to 2 mols of nitrobenzene and 2 to 3 mols of alkali metal hydroxide are used.

3. A process as claimed in Claim 1 or 2, wherein the reaction mixture is filtered before it is acidified.

4. A process as claimed in any one of Claims 1 to 3, wherein the water-soluble alcohol used in carrying out the reaction is an aliphatic alcohol containing 1 to 3 carbon atoms.

5. A process as claimed in any one of Claims 1 to 4, wherein for every part of dihydro ester 1 to 20 parts of water-soluble alcohol are used in carrying out the reaction.

6. A process as claimed in any one of Claims 1 to 5, wherein the water-soluble alcohol used in carrying out the reaction is the same alcohol as is eliminated from the ester group in the course of the hydrolysis.

7. A process as claimed in any one of Claims 1 to 6, wherein an aqueous hydrochloric acid solution of 20 to 40% strength is used as mineral acid solution.

8. A process as claimed in any one of Claims 1 to 7, wherein the reaction is carried out within a temperature range of 60 to 130° C.

9. A process as claimed in any one of Claims 1 to 8, wherein the 2:5-diarylamino-dihydroterephthalic acid ester starting material is first prepared by condensing 1 molecular proportion of a succinylsuccinic acid ester with 2 molecular proportions of an arylamine in a water-soluble alcohol in the presence of a mineral acid as catalyst, and the product so obtained is heated with the nitro-

benzene and alkali metal hydroxide in the same water-soluble alcohol and in the same vessel without intermediate isolation of the said ester starting material.

- 5 10. A process for the manufacture of 2:5-diarylamino-terephthalic acids conducted substantially as described in any one of the examples herein.

11. 2:5-diarylamino-terephthalic acids whenever obtained by the process claimed in any one of Claims 1 to 10. 10

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